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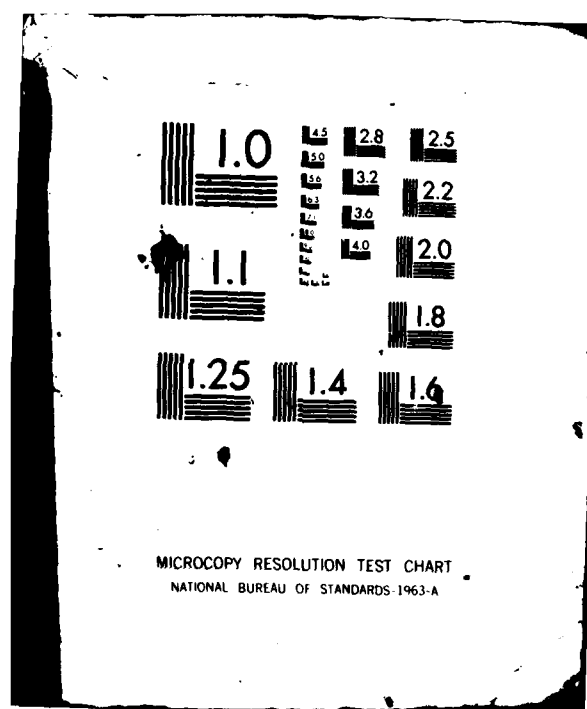
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THESIS

THERMAL MARTENSITIC TRANSFORMATION  
CYCLING IN Cu-Zn-Al SHAPE MEMORY ALLOYS

by

William E. Muesing

March 1982

Thesis Advisor:

A. J. Perkins

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Thermal Martensitic Transformation Cycling  
in Cu-Zn-Al Shape Memory Alloys

by

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Submitted in partial fulfillment of the  
requirements for the degree of

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## ABSTRACT

The effect of multiple thermal cycles between the martensitic phase and parent phase of selected Cu-Zn-Al alloys was studied. As thermal cycling progressed the martensite start temperature ( $M_s$ ), parent phase finish temperature ( $A_f$ ), and the temperature at which the maximum martensitic peak height occurred ( $M_{max}$ ) were all observed to shift upward. The proportion of the sample undergoing thermal transformation decreased with increasing numbers of thermal cycles, as was noted by a decrease of total transformation energy. Examination in a transmission electron microscope found dislocation substructures apparently generated by the martensitic transformations.

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## I. INTRODUCTION

Certain alloys have the unusual ability to recover an original shape after undergoing what would appear to be permanent deformation. These are the so-called Shape Memory Alloys and the property of assuming a former shape is known as Shape Memory Effect (SME). As the shape memory alloy is reverting back to a previous shape, a large force is exerted. Proper development of these alloys and harnessing of this force is offering a new approach to thermally activated controls. Variable orifice jets for automobile carburetors, fluid and gas control valves, thermally operated relays and switches, thermostatic valves, and even heat engines are several possible uses now being studied for shape memory alloys. In the field of medicine there appear to be many applications for these alloys, reliant on their ability to change shape after installation and subsequent warming by the body.

The shape memory effect is a direct result of thermo-elastic martensitic transformation. Unlike other alloys such as steels which undergo martensitic transformations, the shape memory alloy transforms to martensite by forming plates which continue to grow in a continuous manner as temperature is decreased, and as the temperature is raised the plates revert back to the parent phase in an exact reverse path of

the original transformation [Ref. 1]. In most shape memory alloys, there is only one crystallographic route back to the parent phase, while there are several thermal or stress related routes to induce or deform the martensite. So, when one of these alloys is deformed while martensitic, it will regain its original shape as the temperature is raised above that necessary for complete phase transformation to the parent phase ( $A_f$ ). The ability to regain the original shape is due to the nearly exact reconstruction of the original parent crystal, on an atomic level.

Among the shape memory alloys with greatest potential for practical applications, are the Copper-Zinc-Aluminum alloys. The Cu-Zn-Al shape memory alloys are typically about 70 wt.% copper brasses with some aluminum, and the reaction of importance is the transformation of the ordered body centered cubic (BCC) beta phase to a close packed thermoelastic martensitic structure. The Cu-Zn-Al alloys have several advantages over other shape memory materials such as i) relatively low cost, ii) ease of fabrication, and iii) availability of a useful range of martensite transformation temperatures (achieved by slight variations of alloy composition).

The predominant form of thermally induced martensite in the Cu-Zn-Al alloys is the  $\beta'$ , an orthorhombic 9R or 18R variant with ABCBCACAB/A stacking sequence. The transformation from the body centered cubic structure is a diffusionless one in which the martensite inherits the long range

order of the parent phase. The stresses accompanying the transformation do not produce significant plastic deformation or disrupt the continuity between the martensite and parent lattice. As the martensite plates grow, self-accommodation takes place by faulting, resulting in very low elastic strains, i.e., strains not exceeding the elastic limit of the parent lattice.

Deformation of a martensitic Cu-Zn-Al shape memory alloy causes growth, shrinkage and shifting of martensitic plates to an orientation favorable to the applied stress. Some of these alloys have shape memory properties even above  $M_s$ . When strained, stress induced martensite forms from the beta matrix and this stress induced martensite has the same characteristics as the athermal martensite. A lowering of temperature or the application of stress produces the same effect in terms of inducing formations of martensite, while raising the temperature or relieving stress both tend to recreated the parent phase. The key is that martensite may be induced or deformed (to a limit) without destroying the continuity with the parent lattice.

The purpose of this study was to observe the results of multiple thermal cycles between the beta parent (A) and martensitic (M) phases of selected Cu-Zn-Al alloys. By using a differential scanning calorimeter, specific temperatures, which are the milestones of the transformation process, can be recorded during thermal cycling. Thus, slight changes in



the transformation character may be detected as shifts of these temperature milestones, and a study of these shifts coupled with transmission electron microscope observations is intended to lead to better understanding the mechanisms of thermoelastic martensitic transformations.

## II. EXPERIMENTAL PROCEDURES

### A. SAMPLE PREPARATION

The Cu-Zn-Al alloys studied were provided by Delta Materials Research Limited, Ipswich, Suffolk, England. Nominal compositions and reputed  $M_s$  temperatures are given in Table I. These alloys were chosen on the basis of  $M_s$  temperatures; alloy D reputedly existing as the  $\beta$  parent phase at room temperature and alloy E as martensite. The as-received alloys were cut into disks of 3mm diameter and .25 - .40mm thickness. To homogenize and eliminate second phase precipitates while minimizing zinc loss, the samples were sealed in evacuated quartz tubes and annealed at 900°C for 15 minutes. Quenching was accomplished by shattering the quartz tubes in cold water immediately upon removal from the furnace. The resulting grain size in both alloys was large; about .3mm diameter. After annealing, alloy D was observed to have a homogeneous microstructure, consisting entirely of the parent phase. Alloy E appeared to be nearly all martensitic.

Table I. Experimental Alloys (at %)

<u>Alloy</u>	<u>Cu</u>	<u>Zn</u>	<u>Al</u>	<u>Reputed <math>M_s</math></u>
D	66.2	24.8	9.0	263°K
E	68.4	18.6	13.0	323°K

## B. DIFFERENTIAL SCANNING CALORIMETRY

To characterize the martensitic transformation during thermal cycling, a differential scanning calorimeter (Perkin Elmer DSC-2) was utilized. The DSC measures changes in power required to maintain sample and sample holder at the same temperature as a reference holder. Transformation from the beta phase to martensite is exothermic while the reverse transformation, from martensite back to the parent structure, is endothermic. Start and finish temperatures of these reactions are recorded on the chart abscissa. The area under the generated curves is a quantitative measure of the energy transferred to or from the sample, and therefore is directly related to the amount of material undergoing transformation. For alloy D, the DSC was programmed to cycle from 240°K to 300°K, at least 10°K above  $A_f$  and below  $M_f$ . Alloy E was cycled between 260°K and 340°K. A slow heating-cooling rate of 10°K per minute was chosen to ensure thorough transformation during the temperature excursions and to allow easy data reduction from the strip chart recordings.

$M_{max}$  and  $A_{max}$  were defined as the peak temperatures, determined as the temperatures where the maximum transformation rate occurred (maximum displacement on the ordinate in mcal./sec from the alloys' predetermined baselines).  $M_s$  and  $A_s$  were chosen as the temperatures corresponding to the points where the generated curves departed from the pretransformed baselines, while  $M_f$  and  $A_f$  corresponded to the beginning of

the past transformation baseline (Fig. 1a). Measurement of area under these peaks was difficult because the parent phase and transformed martensite have different specific heats and therefore different baselines. The area was estimated as being bordered by the curve and a line connecting the start and finish transformation temperatures (Fig. 1b). Partial thermal cycling was accomplished between the approximate  $M_{\max}$  and  $A_{\max}$  temperatures, as determined by an initial complete thermal cycle (above  $A_s$  to below  $M_f$ , and back to above  $A_f$ ). Transformation peak width was measured at one half the peak height. Polynomial curve fits were generated to better define the shifts of the studied characteristic temperatures.  $A_{\max}$  and  $M_{\max}$  (Fig. 2),  $A_f$  (Fig. 3),  $M_f$  and  $A_s$  (Fig. 4),  $A_{\text{width}}$  (Fig. 8),  $A_{\max} - M_{\max}$  (Fig. 7), and  $A_{\text{height}}$  (Fig. 9) are third order polynomial curves.  $M_s$  (Fig. 3) is a fourth order while  $M_{\text{area}}$  and  $A_{\text{area}}$  (Figs. 5 and 6),  $M_{\text{width}}$  (Fig. 8) and  $M_{\text{height}}$  (Fig. 9) are all second order.

### C. TRANSMISSION ELECTRON MICROSCOPY

The disks were prepared by electropolishing in a 10% KCN solution using 12-18 volts A.C. at room temperature. The finished foils were examined and photographed with a Japan Electron Optics Lab Co., LTD. Transmission Electron Microscope, Model JEM-7. Foils of both alloys were studied prior to and after twenty complete thermal cycles in the DSC, with the goal of observing changes in microstructure that might help to characterize the transformation process.

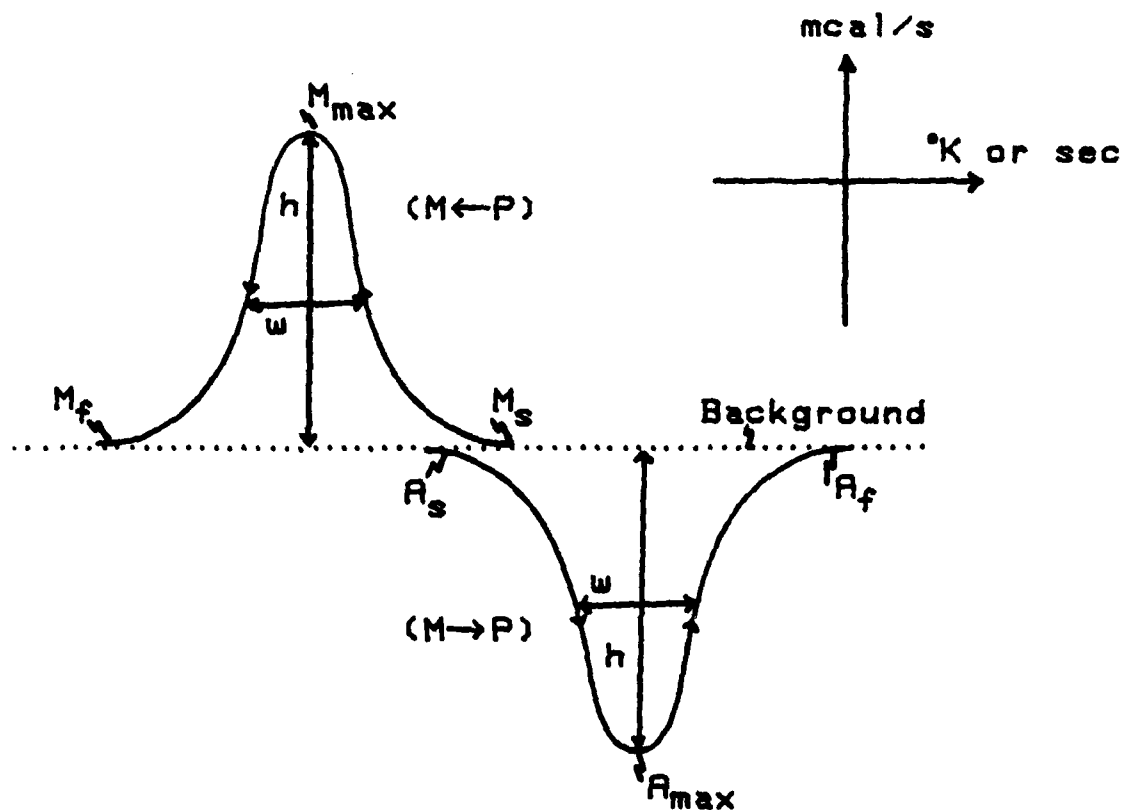


Figure 1a. Example of the determination of  $M_s$ ,  $M_f$ ,  $M_{\text{max}}$ ,  $A_s$ ,  $A_f$ ,  $A_{\text{max}}$ ,  $h$  (peak height), and  $w$  (peak width).

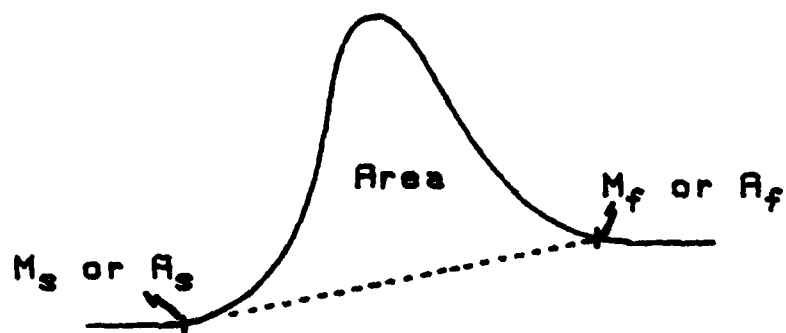


Figure 1b. Estimated area used for the determination of the energy of transformation.

### III. RESULTS AND DISCUSSION

#### A. DIFFERENTIAL SCANNING CALORIMETRY

Much of the data from this study indicates that multiple thermal transformation cycling establishes favored nucleation sites for the martensitic transformation and stabilizes the martensite. For example,  $M_{\max}$ , the temperature at which the greatest quantity of material is undergoing transformation, is seen to shift upward as the number of thermal cycles increases. This is consistent with the establishment of a set of preferred nucleation sites as cycling progresses. As these preferred sites are "learned," martensite nucleates and forms more readily, and  $M_{\max}$  creeps upward. Pops and Massalski [Ref. 2] found that martensitic transformations in Cu-Zn beta phase alloys have two stages, a thermoelastic stage and a "burst" type. The occurrence of the "burst" martensite diminishes and vanishes altogether during multiple thermal cycling. Pops and Massalski have also shown that the formation of "burst" martensite produces lattice defects and some degree of plastic deformation in the parent lattice, and Kajiwara [Ref. 3] has found that thermal cycling introduces dislocations into the matrix phase. Guenin and Gobin [Ref. 4] postulated that zones of instability exist around dislocations and these regions may play an important role in the nucleation of martensite. It is therefore likely

that as cycling progresses, debris from multiple transformations accumulates, and this debris provides more of the preferred martensite nucleation sites. A corresponding decrease of  $A_{\max}$  is not observed because, whereas the parent phase to martensite reaction depends on nucleation, the reverse martensite to parent phase reaction does not; the reversion simply involves shrinkage of the martensite crystalites back to the parent phase. Accompanying the shifting relative values of  $M_{\max}$  and  $A_{\max}$  is a shrinking of the  $A_{\max} - M_{\max}$  hysteresis (Fig. 7). The bulk of the martensite is obviously stable at temperatures above  $M_{\max}$  of the first transition. As nucleation occurs at higher temperatures, the martensitic growth also moves to higher temperatures.

Stabilization of the martensite is evidenced by the tendency of the  $M_s$  and  $A_f$  temperatures to rise with cycling (Fig. 3). Martensite nucleates and grows at higher temperatures during cooling, and around these same nucleation sites it remains to higher temperatures during heating. The increasing width of the martensite and parent phase peaks (Fig. 8) is related to the  $M_s$  and  $A_f$  shifts. All of these factors indicate that the martensite is able to exist over a wider range of temperatures and therefore, thermal cycling has a stabilizing effect on the martensite relative to the parent phase.

As the number of complete thermal cycles increases, it is seen that the amount of transformation taking place during both the cooling and heating cycles decreases (Fig. 6,7).

There are two possible explanations for this noted reduction. The first possibility is that the transformations have become more spread out and the last bits of each transformation are incorporated with the base line and therefore not detected in our data reduction process. This explanation is supported by the general increasing stability of the martensitic phase at higher temperatures. A second and more probable explanation is that less material undergoes transformation after multiple thermal cycles. Either some martensite is retained (on heating above  $A_f$ ) or some parent phase remains after transformation. Li and Ansell [Ref. 5], using electrical resistivity measurements, concluded that it is martensite that is retained as cycling progresses. This would mean that some martensite has become stable, at least within the temperature ranges being used, or else a "blocking structure or force develops which prevents the martensite from transforming back to the parent phase even at temperatures above  $A_f$ . Whichever is the explanation, it is clear that the transformation, especially during the first few cycles, is not a completely reversible process. Some degree of irreversible behavior is taking place and is represented by the decreasing total energy of transformation. Eventually a limit is reached where the total transformation energy remains constant with continued cycling. Further cycles are more completely reversible in nature, that is with a given cycle having the same amount of transformation as the preceding cycle.



During thermal cycling, structures such as secondary peaks develop on the primary peaks. As more thermal cycles are completed, these structures smooth out and eventually blend back into the primary peak. This occurrence is probably not due to "burst" martensite but to a more macroscopic smoothing out of the transformation kinetics. An analogy could be made to creating a trail through initially virgin underbrush. The first time the path is taken travel is difficult. But, upon using the route several times, the trail is more and more established until eventually steady progress is made while traveling it, and no further significant improvements in the trail are possible.

Partial thermal cycling between (approximately) the  $A_{\max}$  and  $M_{\max}$  temperatures demonstrated that the proportion of material not transforming during the partial cycles would, upon completion of partial cycling, transform at a different temperature than the previously active material (Table II, III). Secondary peaks occurred approximately  $5^{\circ}\text{K}$  higher than the primary  $A_{\max}$  peak and  $5^{\circ}\text{K}$  lower than the primary  $M_{\max}$  peak. Some of the alloy evidently had not "learned" the preferred nucleation sites or the transforming material was creating stresses or substructures that retarded the transformation of the rest of the metal.

To examine both of these theories, a sample, after undergoing partial thermal cycling, was then cycled ten complete times. Partial cycling was again accomplished and once more

Table II. Partial Cycling Experiment 1

ONE COMPLETE CYCLE (  $A_f$  to  $M_f$  to  $A_f$  )

$\frac{M_{\max}}{261.8^{\circ}\text{K}}$	$\frac{A_{\max}}{274.6^{\circ}\text{K}}$
--	--

40 PARTIAL CYCLES ( $M_{\max}$  to  $A_{\max}$  to  $M_{\max}$ )  
FOLLOWED BY COOLING FROM  $A_{\max}$  TO BELOW  $M_f$

2 M PEAKS

$\frac{M_{\max 1}}{266.5^{\circ}\text{K}}$	$\frac{A_{\max 2}}{261.2^{\circ}\text{K}}$
--	--

HEATING TO ABOVE  $A_f$

2 A PEAKS

$\frac{A_{\max 1}}{275.1^{\circ}\text{K}}$	$\frac{A_{\max 2}}{281.0^{\circ}\text{K}}$
--	--

COOLING BELOW  $M_f$

1 M PEAK

$\frac{M_{\max}}{265.5^{\circ}\text{K}}$
--

Table II. (Cont'd)

HEATING ABOVE  $A_f$

1 A PEAK

$$\frac{A_{\max}}{275.8^{\circ}\text{K}}$$

10 COMPLETE THERMAL CYCLES

$$\frac{M_{\max 10}}{266.0^{\circ}\text{K}}$$

$$\frac{A_{\max 10}}{276.5^{\circ}\text{K}}$$

40 PARTIAL CYCLES FOLLOWED BY COOLING  
FROM  $A_{\max}$  TO BELOW  $M_f$

2 M PEAKS

$$\frac{M_{\max 1}}{267.1^{\circ}\text{K}}$$

$$\frac{M_{\max 2}}{264.2^{\circ}\text{K}}$$

HEATING ABOVE  $A_f$

2 A PEAKS

$$\frac{A_{\max 1}}{276.2^{\circ}\text{K}}$$

$$\frac{A_{\max 2}}{281.6^{\circ}\text{K}}$$

Table II. (Cont'd)

COOLING BELOW  $M_f$

1 M PEAK

$$\frac{M_{\max}}{266.1^\circ\text{K}}$$

HEATING ABOVE  $A_f$

1 A PEAK

$$\frac{A_{\max}}{276.5^\circ\text{K}}$$

Table III. Partial Thermal Cycling Experiment 2

ONE COMPLETE CYCLE

$$\frac{M_{\max}}{262.0^{\circ}\text{K}}$$

$$\frac{A_{\max}}{273.9^{\circ}\text{K}}$$

40 PARTIAL CYCLES FOLLOWED BY  
HEATING TO ABOVE  $A_f$

2 A PEAKS

$$\frac{A_{\max\ 1}}{273.9^{\circ}\text{K}}$$

$$\frac{A_{\max\ 2}}{275.4^{\circ}\text{K}}$$

COOLING BELOW  $M_f$

1 M PEAK

$$\frac{M_{\max}}{262.8^{\circ}\text{K}}$$

HEATING ABOVE  $A_f$

1 A PEAK

$$\frac{A_{\max}}{273.7^{\circ}\text{K}}$$

sets of two peaks resulted. Any preferred nucleation sites or transformation paths "learned" from the complete thermal cycling were lost or forgotten as partial cycling commenced. This suggests that the latter idea of some type of inhibitor to the transformation is developing during the cycling. It is also interesting to note that if, after partial cycling the sample is directly heated above  $A_f$ , all memory of the secondary peaks in the cooling martensitic transformation and also in the heating, parent phase transformation, is lost. The same is not true if the sample is directly cooled to below  $M_f$  after partial cycling; in this case two peaks will still develop when heating to above  $A_f$ . This indicates that when the parent lattice is reconstructed during the first full heating cycle after partial cycling, it so resembles the original parent lattice that whatever caused the secondary peaks to develop has been eliminated. Secondary peaks can only be regenerated with further partial cycling.

To briefly examine the effects of cold working the beta phase brass on transformation cycling, several disks of alloy D were reduced 10%, i.e., rolled to approximately 90% of their original thickness. No response whatsoever was observed during thermal cycling within the original temperature limits ( $240^{\circ}\text{K}$  -  $300^{\circ}\text{K}$ ) or even at temperatures up to  $600^{\circ}\text{K}$ . It has been noted [Ref. 6] the plastic deformation of beta phase brass can lower the  $M_s$  up to  $50^{\circ}\text{K}$ . If this was the case, the transformation peaks may have been below the lower temperature

limit used and naturally, no peaks were generated. Examination of the deformed specimens in the TEM found that the resulting microstructure after the massive deformation contained a great deal of martensite. If the martensite was reverting back to the parent phase during heating cycles, the transformation was so spread out it cannot be distinguished from the DSC baseline. It appeared, however, from lack of evidence to the contrary, that the martensite was locked in and retained during cycling. Whether the parent phase is retained or undergoes transformation at low temperatures was not determined.

#### B. TRANSMISSION ELECTRON MICROSCOPY

Uncycled samples of alloy D consist, for the most part, of the homogeneous parent phase at room temperature, with low dislocation density (Micrographs 1,2). Delaey, Perkins, and Massalski [Ref. 7] have concluded the mottling or tweed like appearance, observed frequently here in both cycled and uncycled specimens, is due to a very fine precipitate and resulting surface-etch pitting during electropolishing. Scattered martensitic plates, probably formed during electropolishing, were also observed in the uncycled parent phase. Micrograph 3 reveals a number of martensite plates on different habit plane variants, interacting at an early stage of growth. In Micrograph 4, a subtle change in habit plane is noted at a very early stage of growth. Martensite

plates appear to be developing in association with an array of imperfections in Micrograph 5. This situation may constitute the preferred nucleation site model discussed previously.

The most interesting feature observed in the thermally cycled D alloys were the abundance of dislocations and dislocation tangles (Micrographs 6-10). These photo-micrographs tend to confirm that dislocations are generated during thermal cycling. A higher dislocation density brings about more dislocation interactions and local lattice strains associated with the observed tangles and groupings. These dislocations constitute irreversible features introduced by the thermal cycling process. It is speculated here that these dislocation structures or their resulting strain fields may be responsible for the noticeable incomplete transformation occurring after cycling, functioning either to stabilize a phase or block its transformation.

In some cases (Micrographs 11-13) we find dislocations arrayed on parallel slip planes. New martensite plates are also observed to occasionally pair up on parallel planes (Micrograph 14).

The cold worked parent phase is a complex collection of phases and debris (Micrographs 15-21). It would be expected that this alloy would be entirely parent phase but it is seen that extensive amounts of martensite are interspersed with the parent structure. Large numbers of dislocations and



other remnants from the plastic deformation are present in both the parent and martensite lattices. As was stated earlier, no transformation peaks are observed for these specimens. Something is inhibiting the regular thermal transformation of this alloy. High densities of dislocations are common to the strained alloy and the thermally cycled alloyed.

Uncycled alloy E was largely martensite as expected but did contain regions of parent phase (Micrographs 22-25). This is expected since both  $M_s$  and  $M_f$ , and  $A_s$  and  $A_f$  bracket room temperature. Dislocations (Micrograph 22) and faulting (Micrograph 23) were noted in the martensite microstructure. Few dissimilarities between the thermally cycled and uncycled alloy E were observed (Micrographs 26-30). If complete thermal cycling had occurred, it would be reasonable to expect dislocation tangles to be present as observed in alloy D, but few were found. It is therefore probable that much of alloy E is not transforming during thermal cycling. This would confirm the exceptionally small peaks generated by the DSC during cycling. No explanation is offered for this phenomenon.

#### IV. CONCLUSIONS

As a result of multiple thermal cycles,  $M_s$ ,  $A_f$ , and  $M_{max}$  all rise. This is due to the development of preferred sites for the nucleation of martensite and or the stabilization of martensite at higher temperatures. In addition, the energy of transformation decreases as the number of completed cycles increases, indicating that less of the material undergoes transformation. This is most likely due to the retention of martensite above  $A_f$ . Partial thermal cycling accomplished between  $A_{max}$  and  $M_{max}$  produces two M peaks or A peaks, demonstrating that the proportion of the sample not transforming either does not "learn" the preferred nucleation sites and so does not stabilize that proportion of the martensite at higher temperatures, or more likely its reaction is inhibited by obstacles created by the transforming material. In either case the obstacles disappear after heating above  $A_f$ . Transmission electron microscopy reveals irreversibilities in the forms of dislocations and dislocation structures. These dislocations may in some way be connected with the specified temperature shifts and decreasing transformation energy. The transformation becomes more completely reversible from cycle to cycle as thermal cycling progresses.

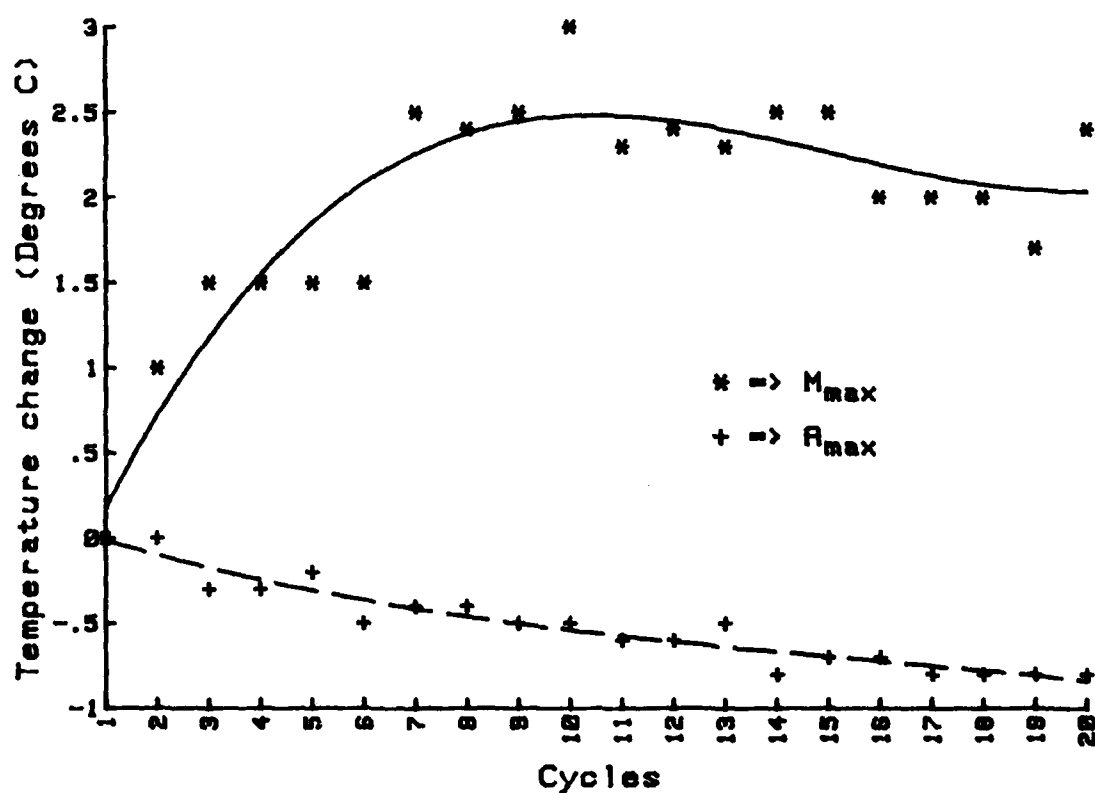


Figure 2. Shifting of the M and A temperatures at which maximum transformation is occurring ( $M_{\max}$  and  $A_{\max}$ ) relative to the corresponding temperatures of the first complete thermal cycle, vs. the number of completed thermal cycles.

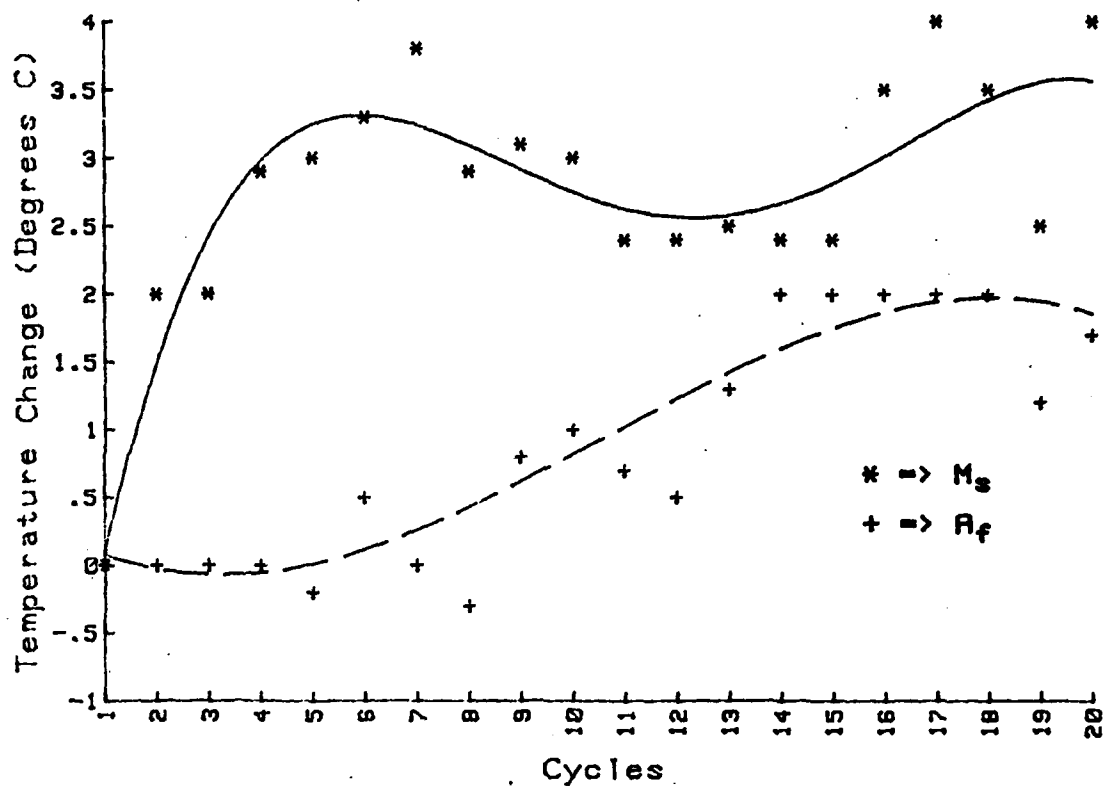


Figure 3. Shifting of the martensite start temperature ( $M_s$ ) and the parent phase finish temperature ( $A_f$ ) relative to the corresponding temperatures of the first thermal cycle, vs. the number of completed thermal cycles.

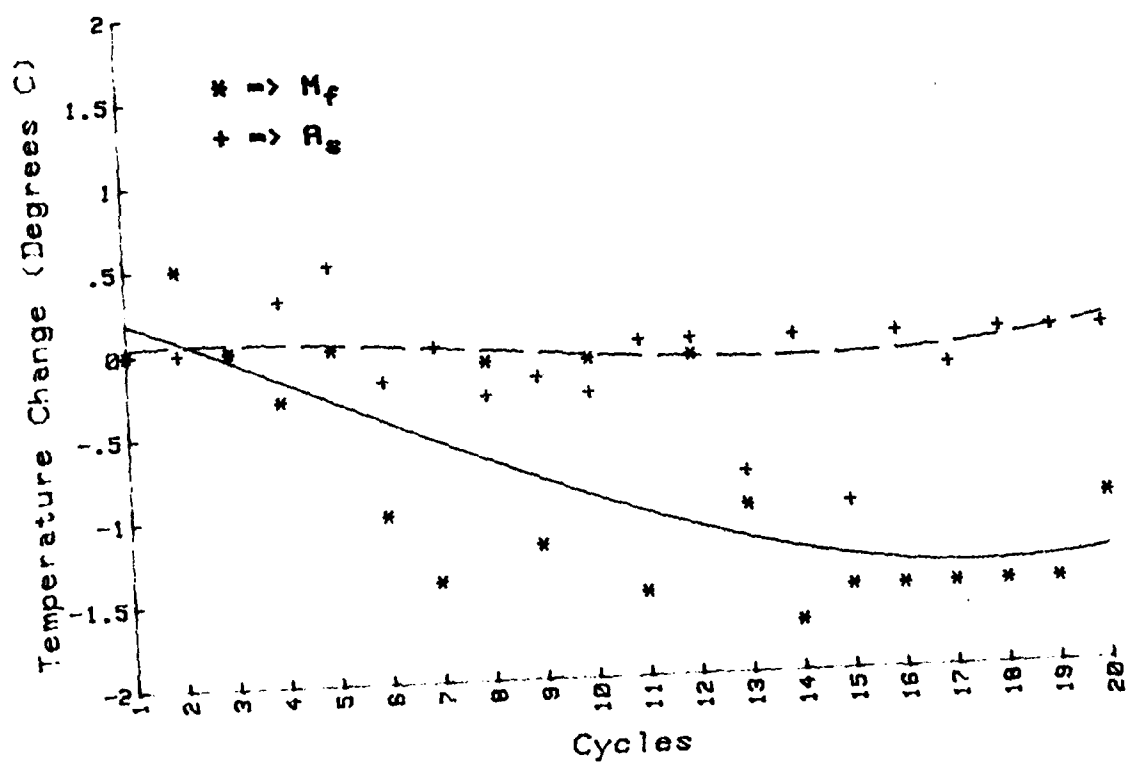


Figure 4. Values of the martensite finish temperature ( $M_f$ ) and parent phase start temperatures ( $A_s$ ), relative to the corresponding temperatures of the first thermal cycle, vs. the number of completed thermal cycles.

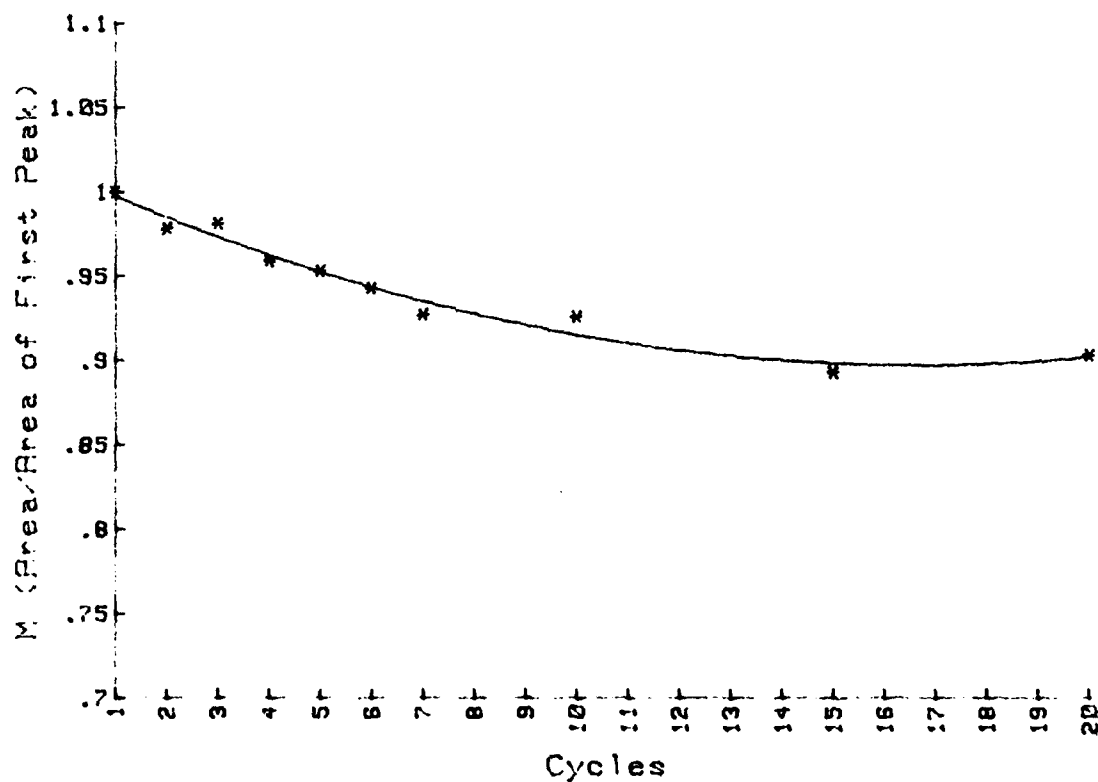


Figure 5. Energy of transformation (represented by area) of the parent phase to martensite reaction divided by that of the first cooling cycle peak, vs. the number of completed thermal cycles.

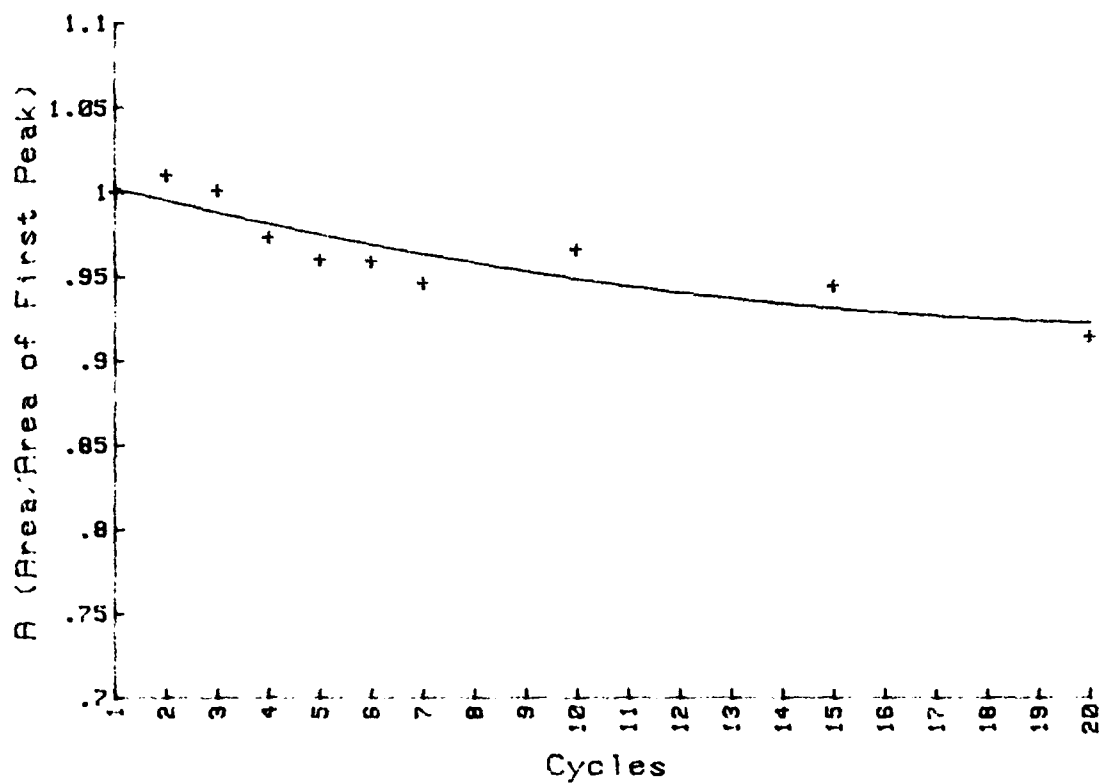


Figure 6. Energy of transformation (represented by area) of the martensite to parent phase reaction divided by that of the first heating cycle, vs. the number of completed thermal cycles.

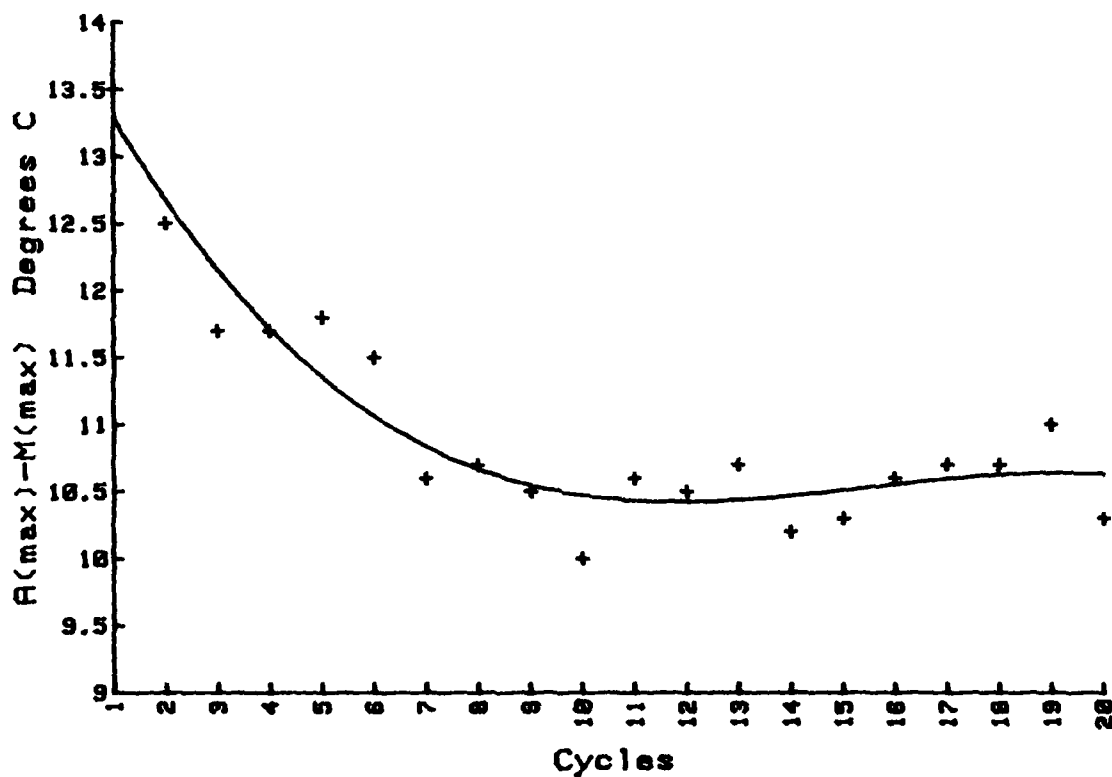


Figure 7. Difference between the transformation peak temperatures ( $A_{\max} - M_{\max}$ ) vs. the number of completed thermal cycles.



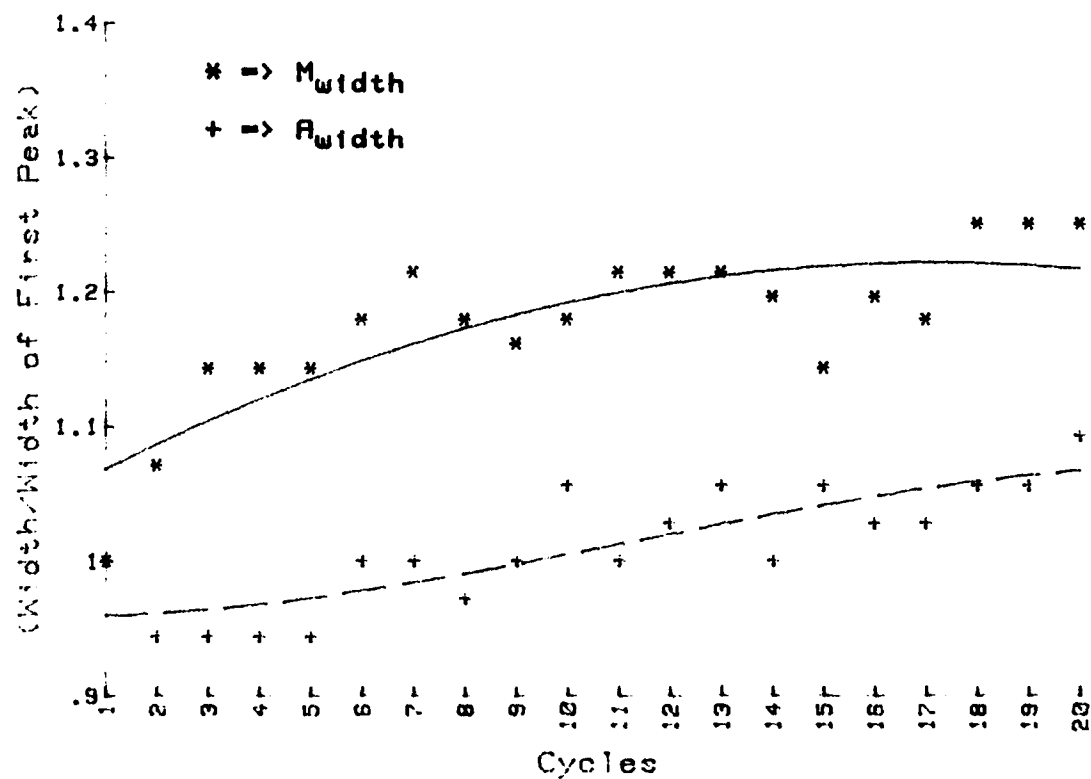


Figure 8. Value of the M and A peak widths, divided by the corresponding measured widths of the first transformation peaks, vs. the number of completed thermal cycles.

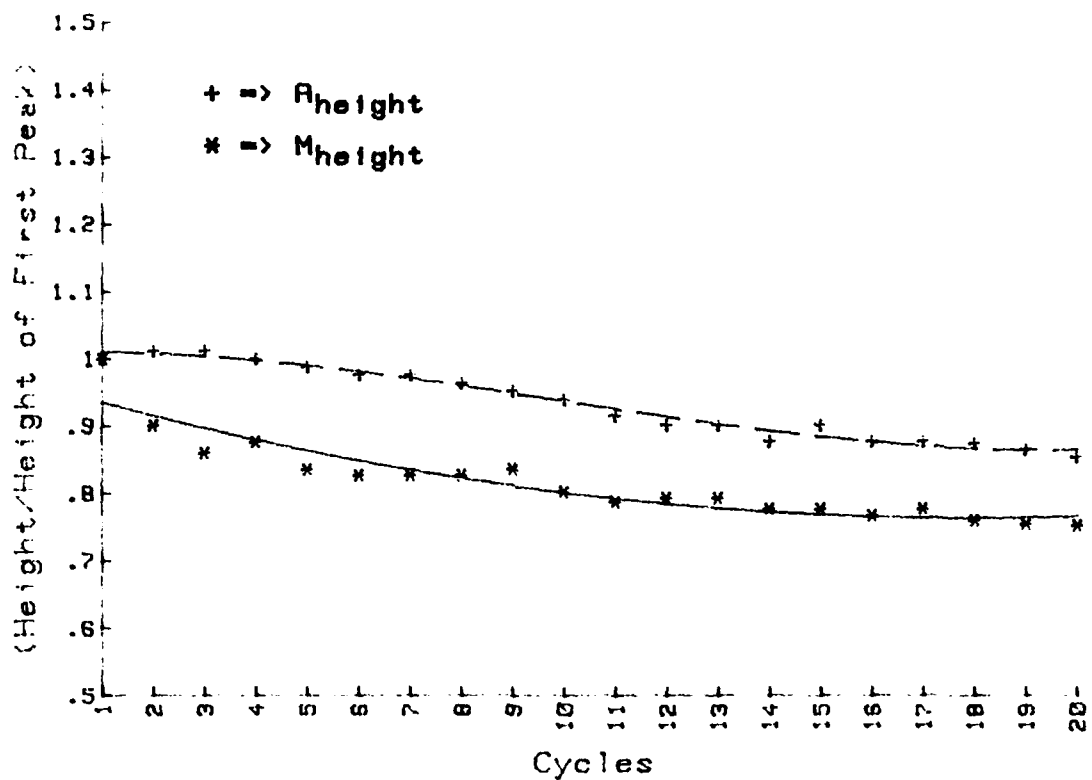
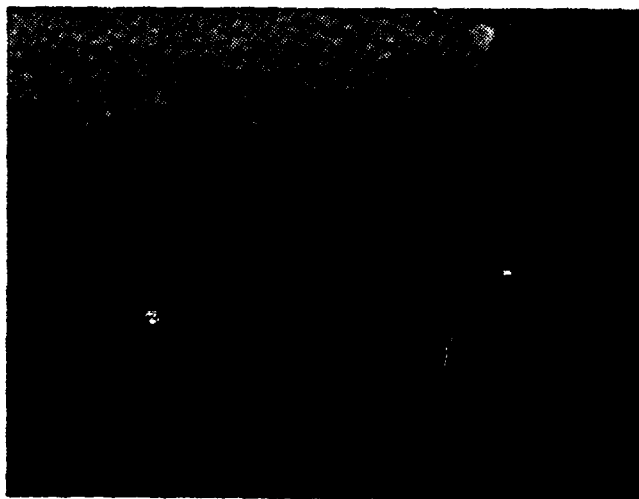
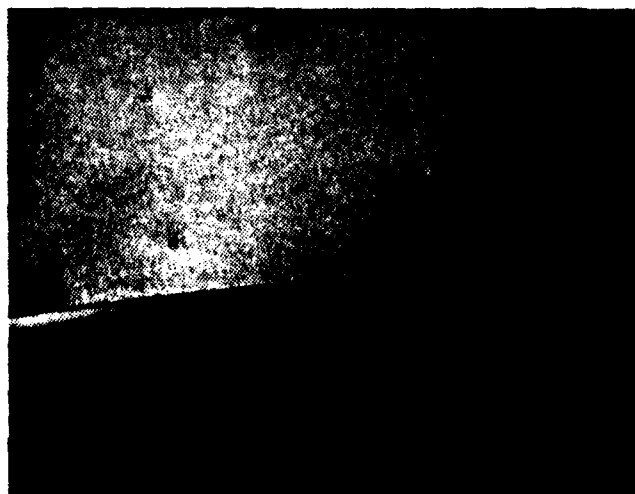


Figure 9. Values of the M and A peak heights, divided by the corresponding measured heights of the first transformation peaks, vs. the number of completed thermal cycles.



Micrograph 1. Alloy D annealed and quenched, prior to thermal cycling. The mottling observed in the beta phase is a result of selected etching during electropolishing caused by a very fine precipitate. x22,000



Micrograph 2. Alloy D annealed and quenched, prior to thermal cycling. The tweed-like pattern observed in Micrograph 1 is in contrast in only one of the two grains separated by a grain boundary. Note the dislocation density appears to be low in these precycled specimens. x12,500



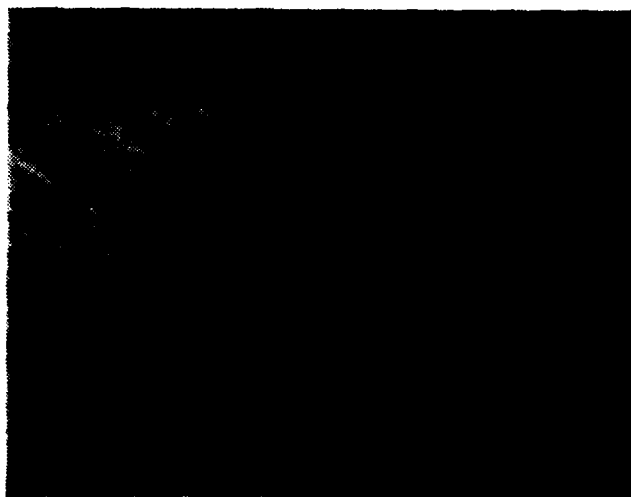
Micrograph 3. Alloy D. The martensite plates observed here are generated by the electropolishing treatment. The martensite plate seen near the pointer may be changing habit planes after considerable growth. x10,000



Micrograph 4. Alloy D. Martensitic plate with a minute change in habit plane occurring soon after nucleation. x14,000



Micrograph 5. Alloy D. Martensite plates originating from an array of lattice defects, which may possibly serve as preferred nucleation sites. x12,500



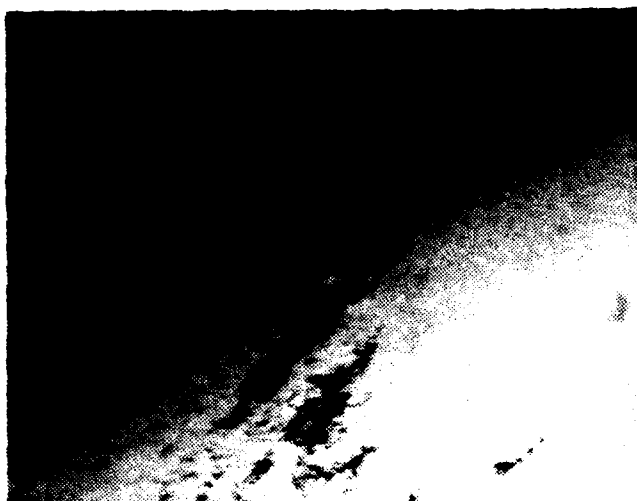
Micrograph 6. Alloy D, annealed and quenched, after 20 complete thermal cycles. This dislocation substructure is formed as a result of the transformations brought on by thermal cycling. x27,000



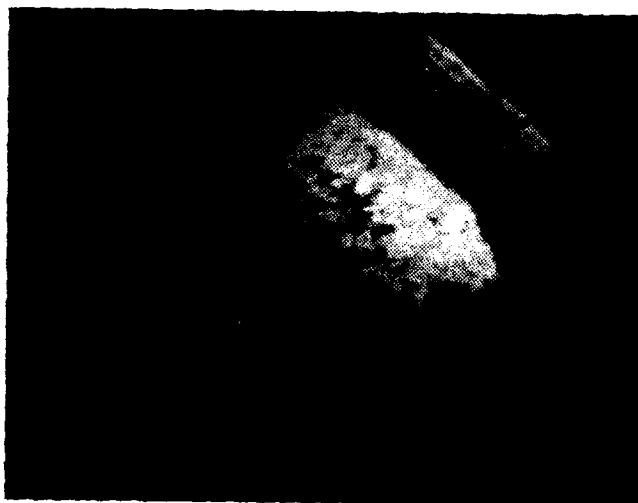
Micrograph 7. Alloy D, annealed and quenched, after 20 thermal cycles. This is the same region seen in Micrograph 6. Dislocations are observed both forming a substructure and as individual defects in the matrix. x10,000



Micrograph 8. Alloy D, annealed and quenched, after 20 thermal cycles. Dislocation arrays formed during thermal transformation cycling. x27,000



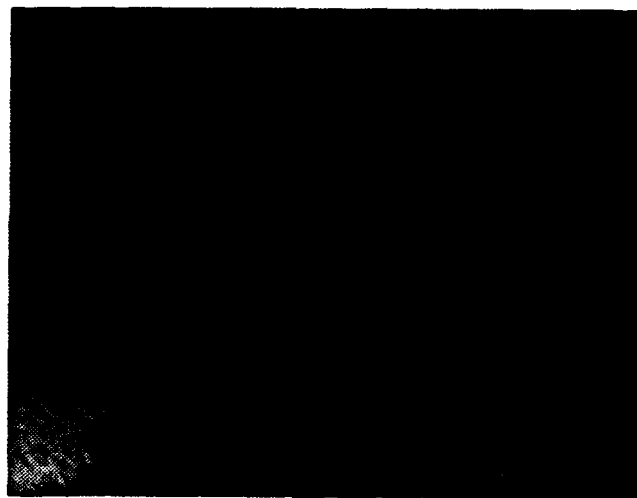
Micrograph 9. Alloy D annealed and quenched, after 20 thermal cycles. Dislocation substructure formed during thermal transformation cycling. x12,500



Micrograph 10. Alloy D annealed and quenched, after 20 thermal cycles. Dislocations generated during the martensitic transformations are observed to congregate in the parent matrix. x10,000



Micrograph 11. Alloy D annealed and quenched, after 20 thermal cycles. Dislocations arrayed on parallel slip planes. x30,000



Micrograph 12. Alloy D annealed and quenched, after 20 thermal cycles. Several dislocations are seen to stack up on similar slip planes. x10,000

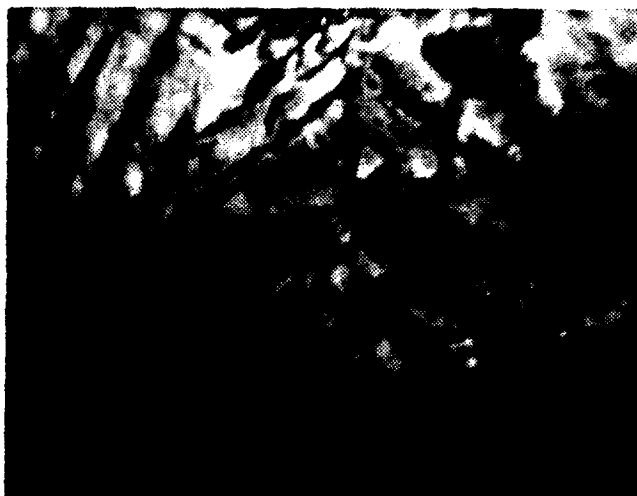




Micrograph 13. Alloy D annealed and quenched, after 20 thermal cycles. Dislocations highlighted on a contour line, are stacked up on parallel slip planes. x11,000



Micrograph 14. Alloy D annealed and quenched, after 20 thermal cycles. Martensite plates, likely generated by electropolishing are observed to exist on parallel planes. x30,000



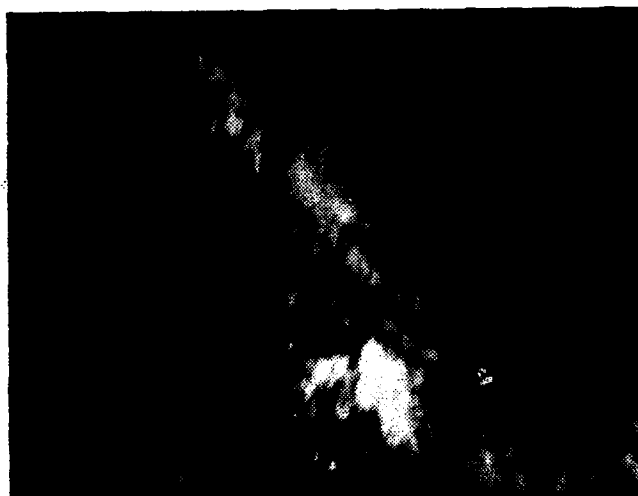
Micrograph 15. Alloy D annealed, quenched and rolled to about 90% of original thickness. A disarray of martensite plates and dense dislocation structure are present with the parent phase. x30,000



Micrograph 16. Alloy D annealed, quenched and rolled to approximately 90% of original thickness. A fairly large region of beta phase, containing a high dislocation density, is observed here. x18,000



Micrograph 17. Alloy D annealed, quenched and rolled to approximately 90% of original thickness. Martensite plates in early stages of growth are seen forming against a background characteristically caused by severe deformation. x16,000



Micrograph 18. Alloy D annealed, quenched and rolled to approximately 90% of original thickness. Martensite is observed forming at different orientations. x10,000



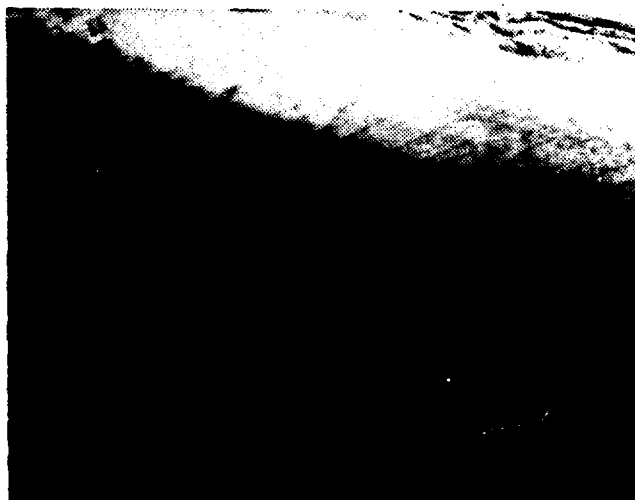
Micrograph 19. Alloy D annealed, quenched and rolled to about 90% of original thickness. Martensite is seen to be branching out into the matrix from an existing martensite plate. Note the similar orientation of the martensite branches. x8,000



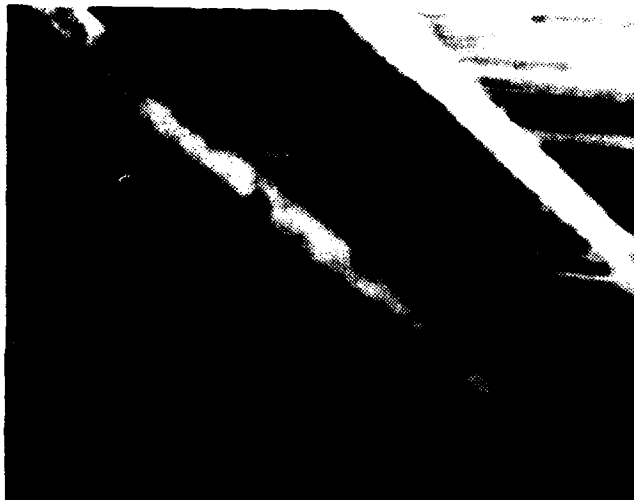
Micrograph 20. Alloy D annealed, quenched and rolled to approximately 90% of original area. The martensite plates are separated by regions of parent phase. x24,000



Micrograph 21. Alloy D annealed, quenched and rolled to approximately 90% of original thickness. This micrograph depicts the severe deformation and retained martensite resulting from cold working the beta phase. x34,000



Micrograph 22. Alloy E annealed and quenched, prior to thermal cycling. Quenching alloy E from the beta phase is equivalent to one half a thermal cycle. Note the arrayed dislocations in this martensite plate. x15,000



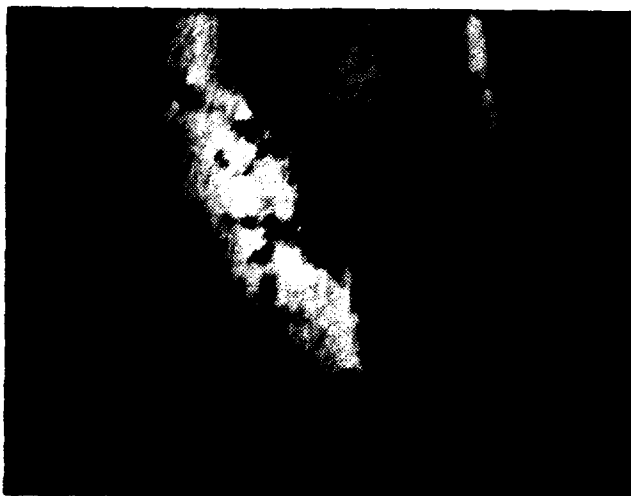
Micrograph 23. Alloy E annealed and quenched, prior to thermal cycling. The martensite plates are observed to be faulted.  
x24,000



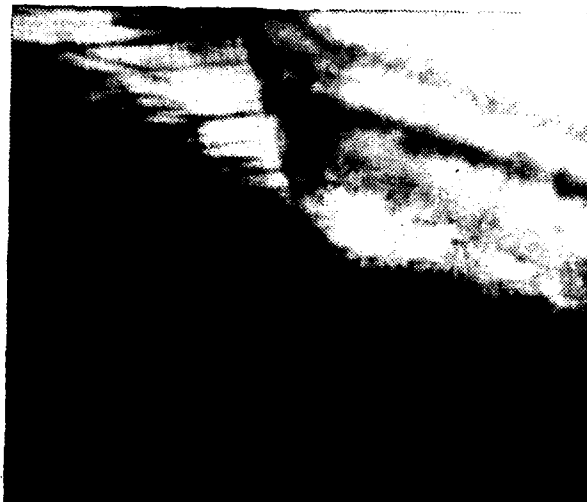
Micrograph 24. Alloy E annealed and quenched, prior to thermal cycling. The junction of several self-accommodating martensite plates in a plate group is seen here. x12,500



Micrograph 25. Alloy E annealed and quenched, prior to thermal cycling. This region of parent phase is adjacent to a martensitic plate. The dislocations were possibly generated as a result of the adjacent transformation during quenching. x12,500



Micrograph 26. Alloy E annealed, quenched and thermally cycled 20 times. Portions of alloy E are parent phase at room temperature. Here, a dislocation substructure is observed in this parent phase. x10,000



Micrograph 27. Alloy E annealed, quenched and thermally cycled 20 times. Parent phase and a martensite plate are seen in this micrograph. Judging from the lack of a dislocation substructure it is likely that this material is not transforming during thermal cycling. x14,000

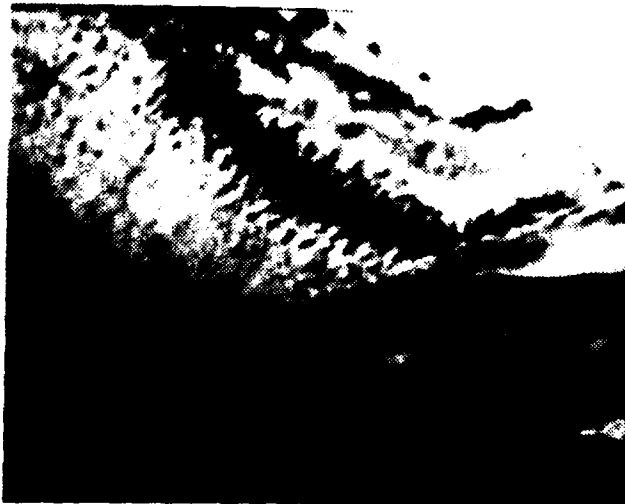


Micrograph 28. Alloy E annealed, quenched and thermally cycled 20 times. Once again an absence of dislocations is noted in the parent phase after thermal cycling. x25,000





Micrograph 29. Alloy E annealed, quenched and thermally cycled 20 times. Some regions of existing parent phase do have dislocation substructures. x10,000



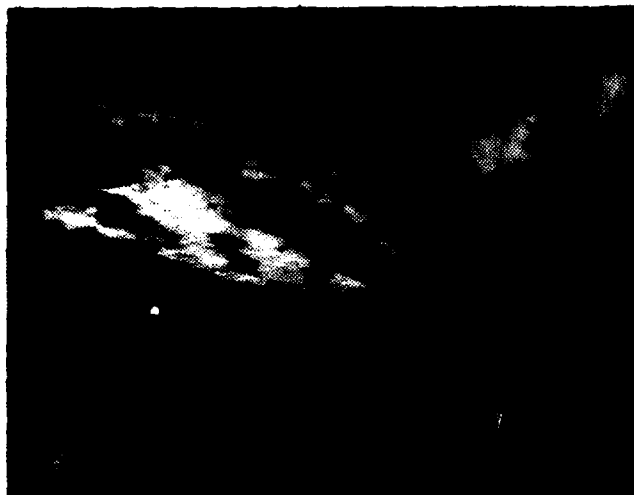
Micrograph 30. Alloy E annealed, quenched and thermally cycled 20 times. The structure of the parent phase is seen here highlighted by a contour line. x27,000



Micrograph 31. Alloy E annealed, quenched and thermally cycled 20 times. Dislocations, resulting from the martensitic transformations are outlined by a contour line. x12,500



Micrograph 32. Alloy D annealed, quenched and thermally cycled 20 times. The growth end of a martensite plate is observed blending into the matrix. x15,000



Micrograph 33. Alloy D annealed, quenched and thermally cycled. Dislocations, generated by martensitic transformations, are observed congregated in tangles. x15,000



Micrograph 34. Alloy D annealed, quenched and thermally cycled 20 times. A martensitic plate root, recognized by the changes in contour lines, is observed in the beta matrix. x12,500

## APPENDIX

The specified transformation temperatures for alloys D and E are listed below. The data listed for alloy D is from the first complete thermal cycle. Data given for alloy E is from the second complete thermal cycle, since no peak was observed during the first half heating cycle.

	<u>ALLOY D</u>	<u>ALLOY E</u>
M <sub>s</sub>	269	296
M <sub>f</sub>	251	276
M <sub>max</sub>	260	287
A <sub>s</sub>	261	293
A <sub>f</sub>	279	305
A <sub>max</sub>	273	299

Calculations of the heats of transformation were based on the maximum area observed during thermal cycling. The borders of the area were estimated (as discussed under Experimental Procedures) and measured with a planimeter. The DSC constant was determined by cycling a standard sample (Indium) through fusion in the DSC.

$$H_t = \frac{K \times (\text{Range}) \times (\text{area})}{(\text{Chart Speed}) \times (\text{Sample Weight})}$$

$K = 2.86 \text{ mm}/(\text{Area in. sq.})$

$H_t$  = Heat of transformation

ALLOY D       $H_t = 2.497 \text{ calories/gram}$

ALLOY E       $H_t = .333 \text{ calories/gram}$

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